Development of a framework to determine mixed plastic waste quality for resource efficiency assessment

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ABSTRACT: Complex waste streams, like municipal solid waste still contain, besides the digestible organic fraction and other residues, valuable and recyclable plastic materials. An extensive amount of these collected plastic waste streams are nowadays incinerated or landfilled. Recycling of mixed plastic waste is a requisite in growing towards a circular economy. In order to obtain a qualitative end product the complex mixture of polymers should be sorted in mono polymeric materials. However, the separation efficiency of the existing technologies is uncertain. For this reason, polymers are often contaminated with one or more other polymer materials. After mechanical recycling this leads to the formation of polymer blend structures. This paper wants to give a clear insight in the development of a framework for the prediction of the quality of mixed plastic waste streams. In such a framework, mechanical properties play a prominent role. In this study the change in mechanical properties of blends consisting of different ratios of LDPE and PET are determined. The impact strength follows a fourth degree equation in function of the LDPE content. Tensile properties can be approached with a second degree equation. The 50/50 wt% composition forms a co-continuous structure, in contrast to the droplet-matrix morphology of the other blends. This co-continuous morphology leads to poor mechanical properties. This information can be used in a resource efficiency indicator allowing prediction of secondary plastics potential.

1 INTRODUCTION

The importance of plastic materials has clearly increased year by year. The increasing use and production of polymers led to issues such as growing plastic waste streams and environmental problems. Stricter legislation pressurizes governments and companies to focus on recycling of these complex waste streams (European Commission, 2018). Nowadays, only 29,7 % of the plastic waste in Europe is recycled (Huysman et al., 2017). Mechanical recycling can be employed to tackle this problem. This re-melting of mixed plastic waste streams has to deal with the immiscibility that exists between the different polymers. This incompatibility leads to phase segregation and causes poor mechanical properties (Utracki, Mukhopadhyay & Gupta, 2014).

The plastic fraction of the municipal solid waste consists of many different polymers (LDPE, HDPE, PP, PET, PA, PS, …). Separation of these polymers is required before recycling. However, separation efficiency is low due to overlapping density ranges, contaminations, foil-like material, physical attachement between the different polymers (glue, multilayers), … Therefore, the separation step is difficult and often costly. A resource efficiency indicator could help to predict the quality of polymer blends (Huysman et al., 2017). This indicator should include different waste quality parameters, like mechanical properties and processability. Such a factor can be a perfect guideline in the fit-for-use separation of mixed plastic waste.

To determine an accurate resource efficiency indicator, the blends are sorted in different classes depending on the compatibility. This miscibility is determined by the interfacial energy between the polymers. The interfacial energy can be approached by Equation 1 (Wu, 1971).

$$\gamma_{12} = \gamma_1 + \gamma_2 - 4\frac{\gamma_{1d}\gamma_{2d}}{\gamma_{1d}+\gamma_{2d}} - 4\frac{\gamma_{1p}\gamma_{2p}}{\gamma_{1p}+\gamma_{2p}} \quad (1)$$

Where γ_{12} is the interfacial energy between polymer 1 and 2. The surface tension of polymer 1 and 2 are represented by γ_1 and γ_2. Subscript d and p are respectively the dispersive and polar components of the surface tension. The interfacial energies of some common polymer pairs are summarized in Table 1 (Huysman et al., 2017, Van Krevelen & te Nijenhuis, 2009).

Table 1: Interfacial Tension for common polymer pairs.

Blend	Interfacial Energy (mN/m)	Class (mN/m)
LDPE/HDPE	0,0023	$0 < \Upsilon 12 < 0,1$
LDPE/PP	0,4135	$0,1 < \Upsilon 12 < 1$
LDPE/PET	9,0013	$1 < \Upsilon 12 < 10$
LDPE/PA	14,1156	$10 < \Upsilon 12$

This study focuses on the development of a framework for the quantitation of mixed plastic waste quality. This work includes the quantitative example of one of the above polymer pairs, namely LDPE/PET, with the focus on its mechanical functional and fail properties. The blends are prepared in an injection moulding machine without preceding compounding step, to approach the industry. The polymers were mixed in different compositions, namely 0 – 5 – 10 – 20 – 50 – 80 – 90 – 95 – 100 wt% LDPE in PET.

2 MATERIALS AND METHODS

2.1 *The framework*

In order to determine the resource efficiency indicator a multi-criteria decision analysis must be performed. Analytical Hierarchy Process (AHP) is one of the available techniques, in which the different criteria are ranked according to preference. This paper introduces such a hierarchy, as can be seen in Figure 1.

In order to be of certain quality, plastic waste streams must meet different criteria. Of course the mechanical properties must meet the requirements of the end-product. Plastic waste streams are more valuable if they have the right colour, no bad smell and do not contain harmful additives. Easy processability also has an influence on the quality.

2.2 *Materials*

Two virgin materials were used in this investigation. The first polymer is LD150AC (ExxonMobil). This LDPE has a melt flow index (MFI) of 0,75 g/10 min (190 °C and 2,16 kg) and melting temperature of 109 °C. The second polymer PET Lighter C93E (Equipolymers) has a melting temperature of 247 °C and a glass transition of 78 °C.

The PET polymer was dried overnight at 120 °C in a vacuum dryer before melt processing. This because of the hygroscopic properties of this material.

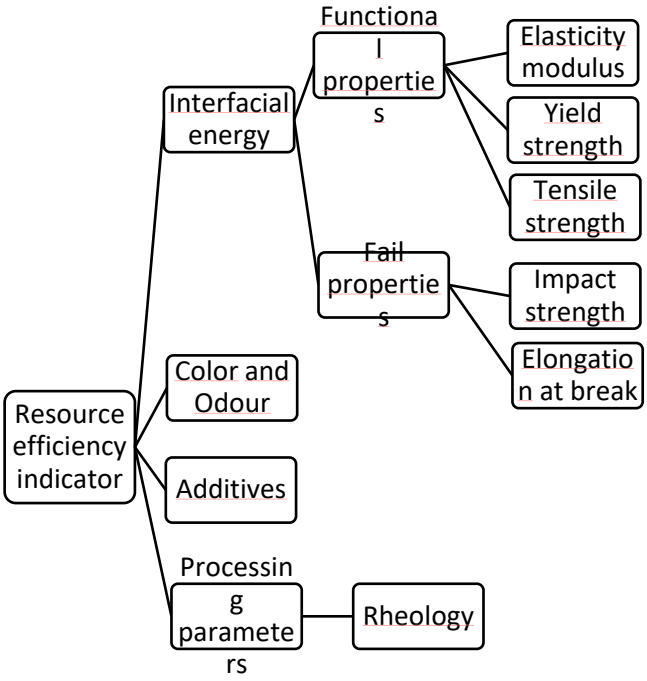


Figure 1. Hierarchy in order to determine the resource efficiency factor for mixed plastic waste.

2.3 *Sample Preparation*

In order to be able to draw up a k-factor, blends that cover the whole composition range (0 wt% to 100 wt%) have to be prepared. In this research blends of the following weight ratios were manufactured: 0 – 5 – 10 – 20 – 50 – 80 – 90 – 95 – 100 wt% PET in LDPE.

The different blend ratios are produced in an injection moulding machine Engel 28T. The polymer pellets were manually mixed before feeding them in the injection moulding machine. The temperature profile used from hopper to nozzle was set as 250 °C, 260 °C, 270 °C and 280 °C. The mould temperature was maintained at 40 °C.

The samples were conditioned at room temperature (23 °C) and 50 % relative humidity for at least one week before characterization.

2.4 *Mechanical Characterization*

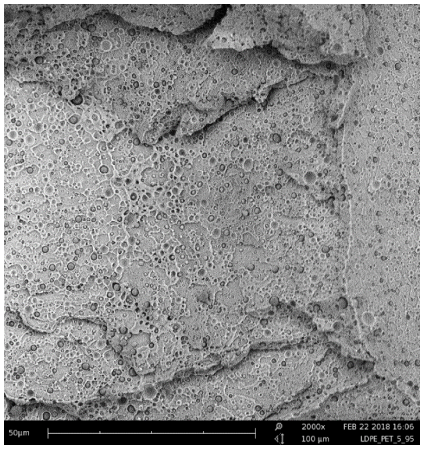
Tensile properties (ISO 527-2) were measured using an Instron 5565 tensile testing machine, with a load cell of 5 kN. For an accurate determination of the strain, the dynamometer was equipped with an Instron clip-on extensometer. A pre-load of 60 N and a crosshead spead of 1 mm/min were set for all the blends. When plastic deformation occurred, the speed was raised to 25 mm/min.

The Charpy impact properties (ISO 179 notched) were measured using a Tinius Olsen IT 503 Pendulum Impact Tester equipped with a hammer with an energy of 5 J.

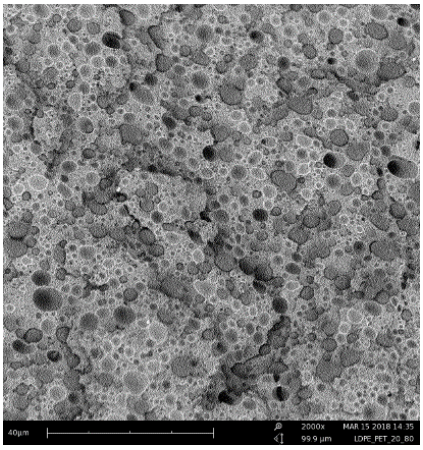
All mechanical tests were executed at room temperature. All reported results are the average of at least ten measurements.

2.5 *Scanning Electron Microscopy*

Scanning Electron Microscopy (SEM) micrographs were taken using a SEM Phenom table top G1. The brittle fracture surfaces of the samples were examined. The brittle fracture was achieved by cryogenic breaking after cooling the samples in liquid nitrogen.



(a)



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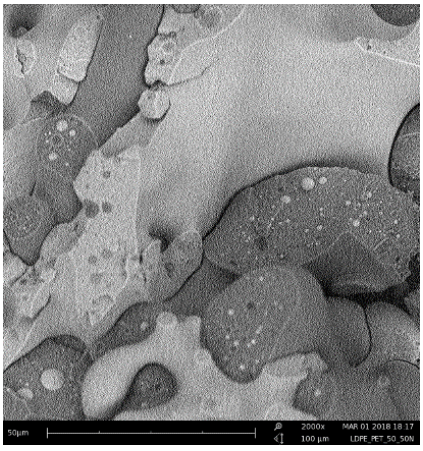

(c)

Figure 2. Representative SEM micrographs of (a) LDPE/PET 5/95 wt% (b) LDPE/PET 20/80 wt% (c) LDPE/PET 50/50 wt% at the same magnification (x2000) obtained after liquid nitrogen fracture.

3 RESULTS AND DISCUSSION

3.1 *Morphological development*

The SEM micrographs in Figure 2 display the dependence of the added weight fraction LDPE on the morphology of a LDPE/PET blend. The SEM images of the LDPE/PET 5/95 (Figure 2 (a)) and LDPE/PET 20/80 (Figure 2 (b)) clearly show a droplet dispersion of the polymer with the lowest weight fraction in a matrix of the other component. This droplet-matrix morphology is also observed in the other blends, except in the 50/50 wt% ratio. At a weight ratio of 50/50 wt%, the LDPE/PET blend exhibit a co-continuous morphology (Figure 2 (c)). Since no use is made of a compatibilizing agent, all blends reveal a rough fracture surface and low interfacial adhesion.

By using the injection moulding machine, without preceding compounding step, it is possible to obtain a relatively good dispersion of the minority polymer component. The lower the weight fraction of the polymer constituting the droplet phase, the finer the dispersion. This can be seen by comparing Figure 2 (a) (LDPE/PET 5/95) with Figure 2 (b) (LDPE/PET 20/80).

Table 2: Tensile properties.

LDPE /PET	Tensile Strength [MPa]	Strain at break [%]	Yield Strength [MPa]
100/0	11,2 ± 0,1	132,1 ± 4,7	6,1 ± 1,0
95/5	11,3 ± 0,2	97,9 ± 11,0	6,3 ± 0,8
90/10	11,3 ± 0,1	82,9 ± 7,9	6,8 ± 0,9
80/20	12,1 ± 0,3	48,9 ± 14,3	9,5 ± 0,6
50/50	20,4 ± 0,4	5,4 ± 0,4	11,7 ± 0,5
20/80	35,8 ± 1,7	13,7 ± 3,8	31,1 ± 1,9
10/90	44,5 ± 3,9	16,0 ± 2,4	38,3 ± 3,7
5/95	52,6 ± 1,1	38,8 ± 20,5	41,8 ± 1,2
0/100	49,5 ± 14,1	35,1 ± 56,6	44,5 ± 14,0

3.2 *Mechanical properties*

The mechanical properties impact strength and tensile modulus are presented in Figures 3 and 5 . The other tensile properties (tensile strength, strain at break and yield strength) are summarized in Table 2. SEM images are used to explain the different trends in mechanical properties.

The results of the impact strength for the different weight ratios of the LDPE/PET blend are visualized in Figure 3. The impact strength enhancement in thermoplastic blends can be ascribed to two competing mechanisms, namely crazing and plastic deformation of the dispersed polymer phase (Palanivelu, Balakrishnan & Rengasamy, 2000). In this research LDPE, which is a ductile material, is mixed with the brittle polymer PET. When small amounts (5 wt%, 10 wt% and 20 wt%) LDPE are present in a PET matrix,

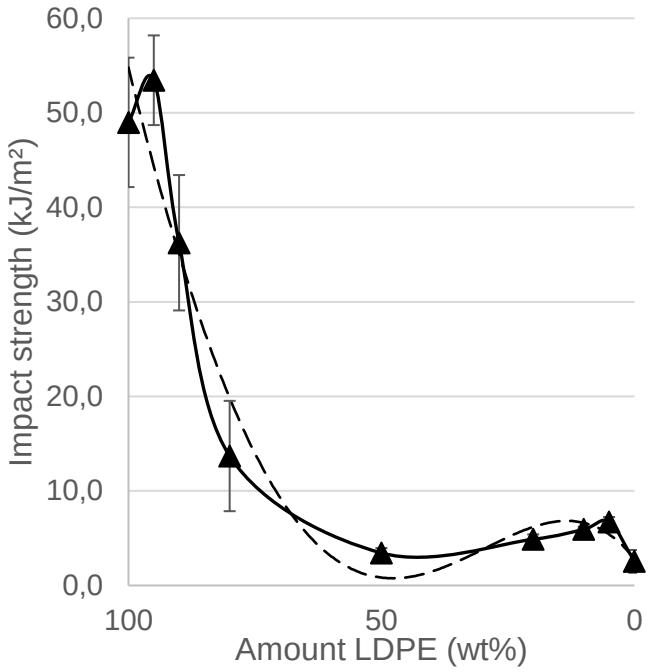

Figure 3. The impact strength in function of the amount LDPE (wt%) in blends of LDPE/PET.

the LDPE acts as an impact modifier. The LDPE polymer is capable of undergoing greater plastic deformation compared to the PET material. Figure 4 (LDPE/PET 10/90 wt%) clearly shows this mechanism, in which the cryogenically caused cracks develop from LDPE droplet to LDPE droplet. Thus, the LDPE droplets inhibit the crack growths, resulting in a higher impact strength compared to the pure PET material. The impact strength is decreasing slightly with increasing amount of LDPE in the PET matrix. This is due to the increasing interfacial surface between the two polymers, wherein the interfacial adhesion between LDPE and PET is poor. The impact resistance reaches a minimum value at 50/50 wt%, as a result of the formation of the co-continuous morphology (largest interfacial surface). When adding a small amount (5 wt%) PET in a matrix of LDPE, the impact

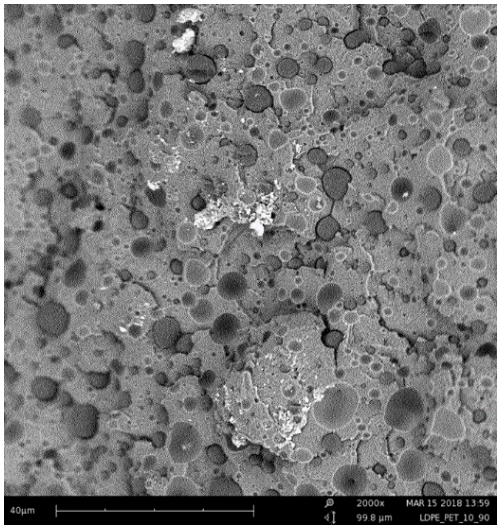

Figure 4. SEM micrograph of LDPE/PET 10/90 wt% at magnification (x2000) obtained after liquid nitrogen fracture.

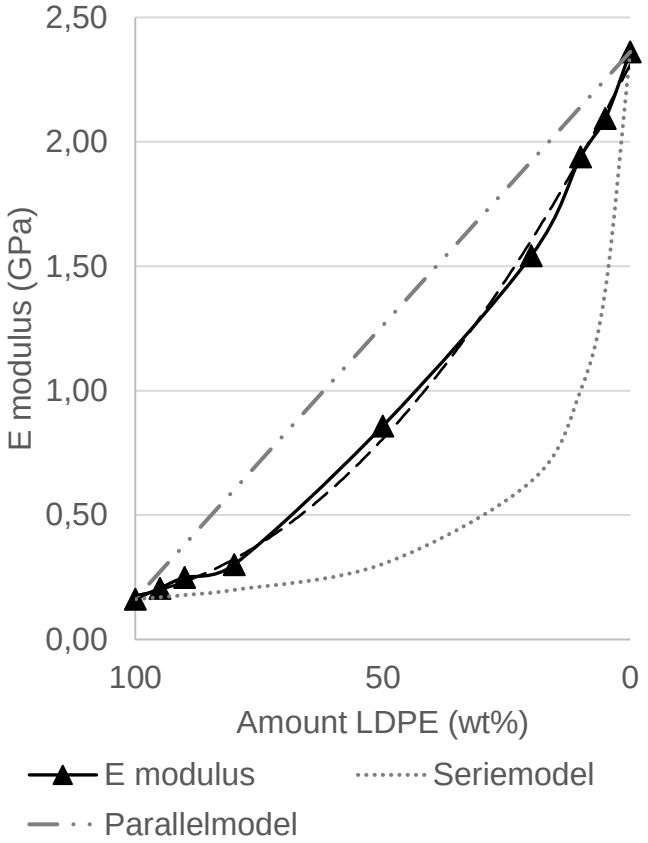

Figure 5. The tensile modulus in function of the amount LDPE (wt%) in blends of LDPE/PET.

strength increases. This enhancement can be attributed to the occurrence of the crazing mechanism. Due to the presence of PET spheres in the LDPE matrix, formation of microvoids is initiated if the material is subjected to deformation. The initiation and propagation of the crazing mechanism allow an energy absorption over a larger surface area (Scheirs, 2000). Mixing of higher amounts of PET (10 and 20 wt%) in LDPE results in a drastic decrease in impact properties. This can again be ascribed to the large contact area between the polymers and the poor interfacial adhesion.

The results of the tensile tests are compared with two theoretical models: parallel model (Equation 2) and series model (Equation 3) (Joseph & Thomas, 2002, Mittal, 2016, Zhimin Xie, Jing Sheng & Zhimin Wan, 2001). In these formulas P_{12}, P_1 and P_2 are respectively the properties of the polymer blend, polymer 1 and polymer 2. The weight fractions of polymer 1 and 2 are represented by x_1 and x_2.

$$P_{12} = x_1 P_1 + x_2 P_2 \quad (2)$$

$$P_{12} = \frac{P_1 P_2}{x_1 P_2 + x_2 P_1} \quad (3)$$

The change of the tensile modulus in function of the amount LDPE is represented in Figure 5. The obtained values for the elastic moduli lie between the two used models. When compared to the parallel

model the deviation between the measured and predicted value is at largest for the 50/50 wt% blend. This can once more be contributed to the larger interfacial surface in combination with the poor adhesion between the two polymers. The pure LDPE is a very elastic and though material, in contrast to stiff PET polymer. Thus, higher amounts of LDPE in the polymer blend will lead to a more flexible material with a high toughness. The other tensile properties (Table 2) follow the same trends.

3.3 *Curve fitting*

With a view to quantitate the k-factor, a regression analysis can be executed. The changes in mechanical properties in function of the weight percentage LDPE is fitted with the most appropriate equations (- - - lines).

The tensile properties can be approached by a second degree function: $E = 0{,}1751x^2 - 38{,}845x + 2310{,}8$. This is presented for the elastic modulus in Figure 4. The impact strength in function of the amount of LDPE (x), follows a fourth degree equation, see Figure 2. The equation is $e_I = -10^{-6}x^4 + 0{,}0005x^3 - 0{,}0346x^2 + 0{,}6819x + 2{,}8081$.

4 CONCLUSION

This study gave an introduction to a possible framework for the quantitation of a mixed plastic waste quality factor. This work focused on the functional and fail properties of a LDPE/PET blend. This polymer mixture is classified as a limited miscible blend, according to the interfacial tension. The blends were produced in an injection moulding machine, without a preceding compounding step, to mimic the industrial recycling process.

In order to investigate the morphology and to explain the results obtained from the tensile and impact tests, SEM-analysis was carried out. From the SEM micrographs, it can be seen that blends of LDPE and PET are constituted of a droplet-matrix morphology. The ratio 50/50 wt% constitutes an exception, as this blend contains a co-continuous morphology.

LDPE will act as an impact modifier in a matrix of PET material. When adding PET in a LDPE matrix, the impact strength will drastically decrease. The impact resistance is minimal at a blend ratio of 50/50 wt% due to the large interfacial surface in combination with the poor interfacial adhesion.

The tensile properties were compared to the parallel and series model for the whole composition range. The measured values lie in between the two models. In comparison to the parallel model, the 50/50 wt% composition again results in the worst properties.
Further research will focus on the determination of the change of mechanical properties in blends consisting of polymers with varying interfacial tension.

5 ACKNOWLEDGEMENTS

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